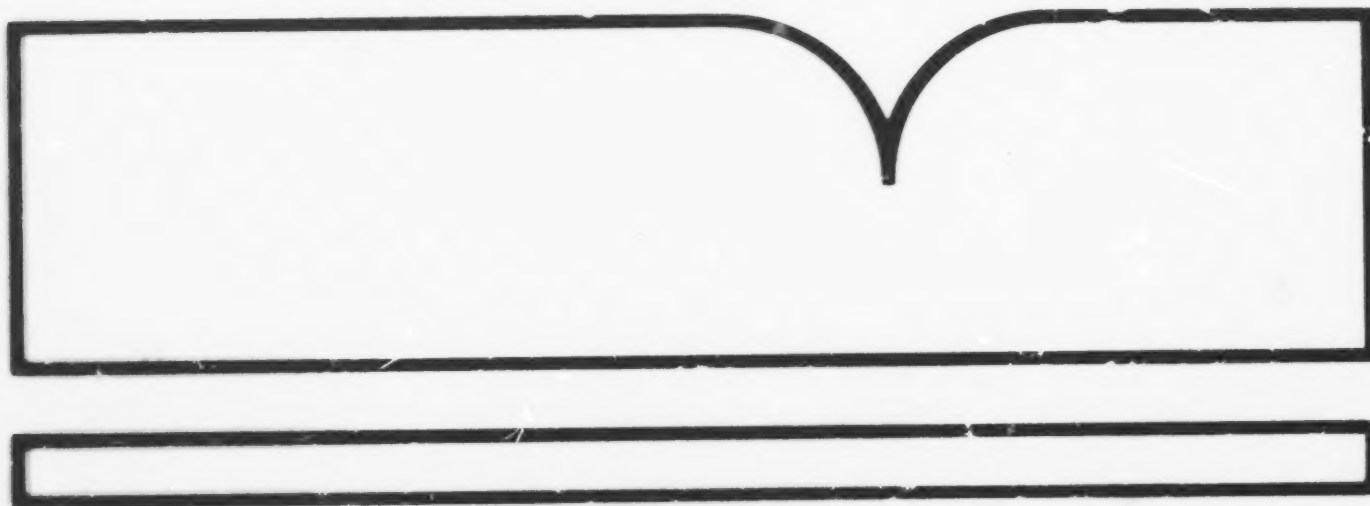


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Large-Scale Preparation of Potassium
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Large-Scale Preparation of Potassium Hydroxide-Modified Silica Gel Adsorbent

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A large-scale method, using custom-made apparatus, is described for making potassium hydroxide-modified silica gel. Batches as large as 2.3 kg can be made in 16 man-hours. A smaller-scale version of the method, requiring no specialized apparatus, is also described. The method can be used to integrate this adsorbent into many sample-enrichment procedures.

The use of base-treated silica gel was widely adopted for the separation of free carboxylic acids from other lipid constituents after it was first reported in 1962 (1). Ramljak and coworkers (2) later reported a linear relationship between the pKa values of various acidic compounds and their R_f values on thin-layer chromatographic plates of KOH-modified silica gel. These earlier applications led Stalling and coworkers (3) to investigate alkali metal hydroxide-modified silica gels (AMSGs) as adsorbents for the enrichment of acidic compounds from environmental samples. In addition to investigating the chromatographic applicabilities of the synthetic AMSGs, Stalling and coworkers characterized the physical and chemical nature of the AMSGs. The results of their investigations using infrared spectroscopy, differential thermal analysis, and x-ray crystallography indicated that their AMSGs closely resembled magadiite, a naturally occurring sodium silicate. Because of the resemblance, the synthetic

adsorbents were labeled lithium-, sodium-, potassium-, and cesium silicates. While the silica gel starting product was transformed only at the particle surface, this did not limit the applicability of the adsorbents, because chromatographic adsorption occurs at the particle surface. In this sense, Stalling and coworkers were correct in referring to these products as alkali metal silicates.

Analytical chemists at the National Fisheries Contaminant Research Center (NFCRC) have discovered the efficacy of these adsorbents for enrichment of nonpolar and basic analytes as well. Potassium silicate (henceforth abbreviated KS) has been incorporated into many enrichment procedures targeting a diverse array of environmental contaminants. Sample matrixes for which KS has proven valuable include fish (and other animal tissue), plant tissues, sediment, soil, and water (4, 5). KS is especially complementary to other adsorbents — silica gel, sulfuric acid-impregnated silica gel, alumina, and dispersed carbon (2, 3) — as well as to size exclusion gel (3, 4). Because KS is more basic than Florisil, it has a greater capacity for acidic compounds, but perhaps for the same reason it has less capacity for neutral and basic compounds. In many situations, chromatographic separations on KS can be substituted for liquid-liquid alkaline wash steps, thereby avoiding emulsions. KS is perhaps most useful for applications requiring the separation of low polarity tar-

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get analytes from acidic or polar co-extracted materials. Many environmental contaminants of worldwide interest (e.g., polychlorinated biphenyls, polycyclic aromatic hydrocarbons, chlorinated dibenzodioxins and dibenzofurans, and many organochlorine pesticides) can be eluted from KS with a dichloromethane-alkane (10 + 90, v/v) eluant while most lipids, pigments, and other potentially interfering materials are strongly retained.

The increased need for KS by analytical chemists at NFCRC led to the development of the large-scale preparation method described here. A medium-scale preparation method requiring only a rotary evaporator is also described. By using a variation of the rotary evaporator method of preparation, the stoichiometry of the reactions can be more precisely controlled, resulting in alkali metal silicates with precisely the desired base-to-silica gel ratios.

METHOD

Cautionary Notes

The preparation of KS (or other alkali metal silicates) can be extremely hazardous. The procedure involves the handling of large volumes of alcoholic KOH. The wearing of protective clothing (impervious to both methanol and base) is recommended for all stages of the procedure involving caustic solutions. Also, safety goggles rather than safety glasses should be worn while working with solutions of methanolic base. Due to the large volumes of methanol used during the procedure, extra precautions against potential fires are warranted. Other recommended safety gear include gloves and masks (to prevent inhalation of dusts of either silica gel or KS). A fume hood should be used.

Overview

In response to requirements for large quantities of KS, a method of preparation was developed that yields ca 2.3 kg adsorbent and requires ca 16 man-hours per batch to produce. This estimate of required time and personnel allows for

tumbling the KS to ensure homogeneity and titration of the KS to verify the degree of alkalinity and batch-to-batch consistency. The apparatus used to make KS is shown in Figure 1. The reaction mixture of base, methanol, and silica gel is contained in a 12 L round-bottom flask. While the flask is partially submerged in a heated water bath, it is rotated by a gear motor having twin drive shafts attached to a collar secured around the neck of the flask. Since our water bath cannot contain water deep enough to support the weight of the flask and its contents, the special rack shown in Figure 1 was designed. The rack supports the weight of the flask, yet the Teflon rollers allow the flask to rotate freely.

Preparation of Reaction Slurry

Combine 4500 mL methanol (pesticide grade, or equivalent) and 1008 g reagent grade KOH pellets in 12 L flask. Plug opening of flask with Teflon stopper, and rotate flask in unheated water bath until base has dissolved. Use of custom-made apparatus for mixing reduces risk of breakage and dissipates heat generated by dissolution of base in methanol.

After KOH has dissolved, add 1800 g silica gel to flask. (We use 70-230 mesh SG-60 from EM Science, activated beforehand at 130°C.) Add silica gel a little at a time, swirl flask, and let each addition of silica gel sink to bottom of solution before adding more. Lumps formed by too-rapid addition of silica gel can persist through later stages of preparation, resulting in KS that is heterogeneous with respect to both texture and KOH distribution. Allow 30 min for addition of 1800 g silica gel.

Rotating Reaction Flask at Elevated Temperature

After addition of silica gel, immediately plug flask with Teflon stopper. Preheat water bath to 55°C, and return flask containing reagent mixture to submerged support rack. Reattach twin drive shafts to collar around neck of flask, and rotate flask 90 min in 55°C water. The gear motor we use rotates the flask at about 60 rpm, a rate that seems to thoroughly mix reaction slurry. Our bath contains 10 cm water, a depth more than adequate to transfer heat to flask contents.

Washing and Drying KS

After 90 min, remove flask from water bath and dry outside surface with paper towel. Use large, custom-made glass column (total capacity ca 7 L) for washing and drying adsorbent. (The dimensions of our column include a lower portion of 40 cm × 10 cm id and an upper reservoir of 20 cm × 14 cm id. A 60/40 female ground-glass opening is at the top.) Tamp plug of glass wool to bottom of column, and insert 25 L polyethylene funnel (Bel Art Products Cat. No. H14716) into mouth. Place 2 L beaker beneath column to collect effluent methanolic KOH. Swirl 12 L flask vigorously until all solid material is suspended in liquid. Then quickly pour as much of slurry as possible into funnel before solid material in flask sinks to bottom of methanolic KOH and is no longer pourable. Repeat these steps until there is no longer enough liquid in flask to resuspend remaining solid material.

Substitute second 2 L beaker for one beneath column. Transfer effluent methanolic KOH that has been collected in first beaker to 12 L flask, and use it to resuspend and transfer any remaining solid material to funnel. Repeat these steps until flask is empty, then similarly use effluent methanolic KOH to wash all solid material remaining in funnel into column. Remove funnel and loosely cover top opening of column with aluminum foil. When liquid level in column has descended to level of top of settled KS, add 600 mL fresh

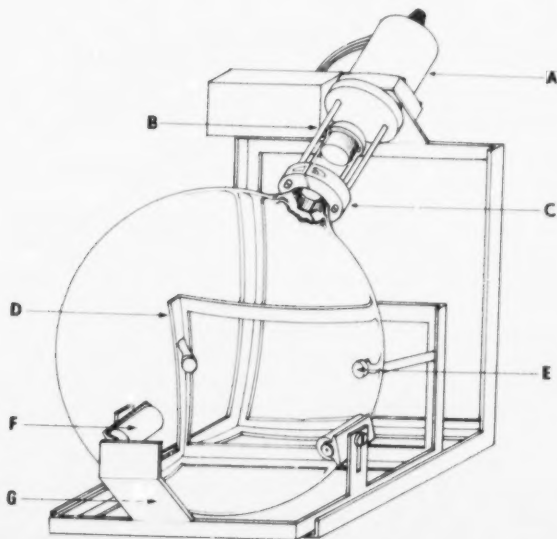


Figure 1. Apparatus for preparing KS in large batches: A, gear motor; B, drive shaft; C, collar affixed to neck of flask, has threaded holes for drive shaft attachment; D, inner rack (32 cm long × 32 cm wide × 20 cm high) which can slide in and out of outer rack (35 cm long × 37 cm wide × 43 cm high); E, Teflon-coated support point; F, Teflon roller; G, Teflon-coated support plate.

methanol to column. Repeat this step twice. When liquid level has descended to top of KS for fourth time, wash KS with three 1 L portions of CH_2Cl_2 (pesticide grade, or equivalent). After most of the third liter of CH_2Cl_2 has run through KS, use 60/40 male ground-glass elbow to connect column to tank of dry nitrogen. Adjust pressure of dry nitrogen to ca 2 psi and maintain flow until outside of column no longer feels cold to touch (ca 18 h), indicating that all CH_2Cl_2 has evaporated. If KS is activated while containing residual CH_2Cl_2 , lumpy product will result.

Activation and Tumbling of KS

Distribute KS among several glass pans so that each pan contains KS to maximum depth of ca 3 cm. Cover pans with aluminum foil and immediately place in 130°C oven for at least 12 h. After activation, recombine KS from pans in 8 L wide-mouth bottle. Cover bottle opening tightly with thin sheet of Teflon or polyethylene. Hold covering material in place with rubber band around neck of bottle. Tumble KS on bottle roller for at least 3 h to ensure that entire batch of KS is homogeneous with respect to base distribution. (After having been washed with methanol, KS at top of column may be slightly less basic than KS at bottom.) After tumbling, return KS to oven for storage. KS is now ready for use, pending favorable outcome of optional titration.

Titration

Titration of alkali metal silicates is a slow process because much of the base is not easily accessible to either acid or water. Once the base is removed from the pores of the silicate, however, its neutralization should be almost instantaneous. In the procedure standardized for titrations of KS, a mechanical shaker and a pH meter are used. One g KS and 25 mL water are combined in 50 mL centrifuge tube, placed in shaker, and shaking is begun immediately. The pH of the suspension increases during all periods of shaking throughout the titration, illustrating the difficulty in accessing the more remotely attached cations. Titration is done with 10% HCl solution, using 1.0 mL syringe to dispense acid between periods of shaking. Since the amount of acid required to neutralize the suspension has been previously estimated, the titration is expedited by initially adding two-thirds of the required total. Even after having been shaken 4 h and having attained a pH of 7, a silicate suspension shows a slow increase in pH if the shaking is resumed. However, any increase in pH at this point represents a negligible quantity of base. Since the main purpose is to verify the batch-to-batch consistency of the KS, we rigidly adhere to 4 h for the titration. The KS product usually contains ca 5 mmol KOH/g KS. To meet our criteria of acceptability, the KS must contain between 4.8 and 5.3 mmol KOH/g KS.

Small-Scale Preparation

Those who do not wish to incur the initial expense of the custom-made apparatus can prepare KS of identical characteristics by a smaller-scale procedure. Quantities of all reagents are reduced by factor of 6, and reaction is carried out in 2 L round-bottom flask. Flask is attached to rotary evaporator (e.g., Brinkmann, Buchi RE120) with which it can be heated and rotated (no vacuum should be applied). A smaller column is used to wash and dry KS.

Variations of Procedure

For applications requiring more precise chromatographic enrichments, especially those involving acidic analytes, a different method for preparing KSs has been devised, which allows for greater control over the stoichiometry of the reactions. Also, KSs of any desired base-to-silica gel ratio (between neutrality and that which results in coalescence of the adsorbent) can be made by this procedure. The silica gel used should have previously been washed with CH_2Cl_2 and then oven activated. The procedure is similar to the scaled-down procedure in that a rotary evaporator is used. After the 90-min reaction time has elapsed, however, the process is as follows:

Turn on vacuum and evaporate methanol. Start with low vacuum, and increase it slowly as danger of bumping diminishes. After most of methanol has evaporated, a sandstorm-like activity will occur in the flask. To avoid getting KS particles in condenser, use evaporator trap (Kontes Cat. No. K570200, containing plug of glass wool) between reaction flask and rotary evaporator. When nearly all methanol has evaporated (sandstorm-like activity has abated), increase water temperature to 90°C. Visually discernible increase of surface tension in condensate on condenser coils signifies that all methanol has evaporated and that water has begun to evaporate. Remove flask from evaporator, and transfer KS to pan for oven activation. It is unnecessary to solvent-wash (assuming reagents are of required purity), titrate, or tumble KSs made by this procedure.

Results and Discussion

The KS produced by either the large-scale or small-scale procedure typically contains 5.0 mmol KOH/g KS. This represents a 1.6-fold greater base-to-silica gel ratio than in the previously produced research adsorbent (3) in which, it was stated, nearly all of the hydroxyl protons had been replaced with K^+ ions. This also represents a 1.6–1.0 molar ratio of adherent K^+ ions on the KS product to hydroxyl groups on the silica gel ingredient (6, 7). Apparently, the excess K^+ ions adhere to the adsorbent by a different mechanism than do the more tightly bound K^+ ions, causing the excess K^+ ions to be more vulnerable to removal by methanol. When KS is washed with methanol, the volume of methanol used greatly influences the degree of alkalinity of the finished product and batch-to-batch reproducibility with respect to the degree of alkalinity.

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